

沙棘叶中鞣质类成分及其抗炎和抗肥胖活性研究

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摘要: 目的 研究沙棘 *Hippophae rhamnoides* 叶的化学成分及其抗炎和抗肥胖活性。方法 采用硅胶、ODS、Sephadex LH-20、MCI CHP20 柱色谱和半制备液相等方法进行分离纯化, 通过波谱分析鉴定化合物的结构。对分离得到的化合物进行体外抑制 RAW264.7 巨噬细胞一氧化氮生成的抗炎活性和抑制 3T3-L1 脂肪细胞三酰甘油蓄积的抗肥胖活性评价。结果 从沙棘叶中分离得到 18 个鞣质类化合物, 分别鉴定为 1,2,6-三-*O*-没食子酰基- β -D-吡喃葡萄糖 (1)、1,3,6-三-*O*-没食子酰基- β -D-吡喃葡萄糖 (2)、1,4,6-三-*O*-没食子酰基- β -D-吡喃葡萄糖 (3)、1,3,4,6-四-*O*-没食子酰基- β -D-吡喃葡萄糖 (4)、1,2,3,6-四-*O*-没食子酰基- β -D-吡喃葡萄糖 (5)、1,2,3,4,6-五-*O*-没食子酰基- β -D-吡喃葡萄糖 (6)、1-*O*-没食子酰基-4,6-(*S*)-六羟基联苯甲酰基- β -D-吡喃型葡萄糖 (7)、1-*O*-没食子酰基-2,3-(*S*)-六羟基联苯甲酰基- β -D-吡喃型葡萄糖 (8)、1,3-二-*O*-没食子酰基-4,6-(*S*)-六羟基联苯甲酰基- β -D-吡喃型葡萄糖 (9)、1,6-二-*O*-没食子酰基-2,3-(*S*)-六羟基联苯甲酰基- β -D-吡喃型葡萄糖 (10)、木麻黄鞣亭 (11)、1,2,3-三-*O*-没食子酰基-4,6-(*S*)-六羟基联苯二甲酰基- β -D-吡喃型葡萄糖 (12)、1,4,6-三-*O*-没食子酰基-2,3-(*S*)-六羟基联苯二甲酰基- β -D-吡喃型葡萄糖 (13)、hippophaenin B (14)、pedunculagin (15)、木麻黄鞣宁 (16)、鞣花酸 (17) 和松醇 (18)。结论 化合物 2、3、5、6、8、10、12 和 13 为首次从该属植物中分离得到, 沙棘叶中的鞣质类化合物具有较强的抗炎活性和抗肥胖活性。

关键词: 沙棘叶; 鞣质; 抗炎; 抗肥胖; 1,3,6-三-*O*-没食子酰基- β -D-吡喃葡萄糖; 1,2,3-三-*O*-没食子酰基-4,6-(*S*)-六羟基联苯二甲酰基- β -D-吡喃型葡萄糖

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Inhibitory effects of tannins from leaves of *Hippophae rhamnoides* and their anti-inflammatory and anti-obesity effects

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Abstract: **Objective** To study the anti-inflammatory and anti-obesity constituents from the leaves of *Hippophae rhamnoides*. **Methods** Several open-column chromatographic techniques and semi-preparative HPLC were used to separate and purify the compounds in *H. rhamnoides*. The structures of isolated compounds were elucidated by the spectroscopic analysis. Their inhibitory effects on nitric oxide production in RAW264.7 cells, and triglyceride accumulation in 3T3-L1 cells were examined. **Results** Eighteen tannins and other compounds were isolated and identified as 1,2,6-tri-*O*-galloyl- β -D-glucopyranose (1), 1,3,6-tri-*O*-galloyl- β -D-glucopyranose (2), 1,4,6-tri-*O*-galloyl- β -D-glucopyranose (3), 1,3,4,6-tetra-*O*-galloyl- β -D-glucopyranose (4), 1,2,3,6-tetra-*O*-galloyl- β -D-glucopyranose (5), 1,2,3,4,6-penta-*O*-galloyl- β -D-glucopyranose (6), 1-*O*-galloyl-4,6-(*S*)-HHDP- β -D-glucopyranose (7), 1-*O*-galloyl-2,3-(*S*)-HHDP- β -D-glucopyranose (8), 1,3-di-*O*-galloyl-4,6-(*S*)-HHDP- β -D-glucopyranose (9), 1,6-di-*O*-galloyl-2,3-(*S*)-HHDP- β -D-glucopyranose (10), casuarictin (11), 1,2,3-tri-*O*-galloyl-4,6-(*S*)-HHDP- β -D-glucopyranose (12), 1,4,6-tri-*O*-galloyl-2,3-(*S*)-HHDP- β -D-glucopyranose (13), hippophaenin B (14), pedunculagin (15), casuarinin (16), ellagic acid (17), and pinitol (18).

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Conclusion Tannins from the leaves of *H. rhamnoides* showed anti-inflammatory and anti-obesity activities. Compounds **2**, **3**, **5**, **6**, **8**, **10**, **12**, and **13** were isolated from this genus for the first time

Key words: *Hippophae rhamnoides* L.; tannin; anti-inflammation; anti-obesity; 1,3,6-tri-*O*-galloyl- β -*D*-glucopyranose; 1,2,3-tri-*O*-galloyl-4,6-(*S*)-HHDP- β -*D*-glucopyranose

沙棘 *Hippophae rhamnoides* L. 为胡颓子科沙棘属的落叶灌木或小乔木，主要分布在丝绸之路沿线国家。我国是世界上沙棘种质资源和蕴藏量最丰富的国家，共有 7 种 7 亚种，广泛分布于我国西北、华北、东北、西南等地，其蕴藏量约占世界沙棘资源的 90%^[1]。

《中国药典》2015 年版收载有沙棘，其果实具有健脾消食、止咳祛痰、活血散瘀的功效，系蒙古族、藏族习用药材。沙棘叶虽然未被《中国药典》所收载，但是国家卫生和计划生育委员会已于 2013 年将沙棘叶作为新资源食品管理。沙棘叶主要含有黄酮类^[2-3]、萜类^[3-4]、鞣质类^[5-6]化合物。沙棘叶具有抗炎^[3]、抗肥胖^[3]、调血脂^[7]、抗氧化^[8]等生物活性。但是沙棘叶的药效物质基础尚未完全清楚，为了进一步明确沙棘叶抗炎和抗肥胖药效物质基础研究，本实验从沙棘叶中分离得到了 18 个化合物，分别鉴定为 1,2,6-三-*O*-没食子酰基- β -*D*-吡喃葡萄糖 (1,2,6-tri-*O*-galloyl- β -*D*-glucopyranose, **1**)、1,3,6-三-*O*-没食子酰基- β -*D*-吡喃葡萄糖 (1,3,6-tri-*O*-galloyl- β -*D*-glucopyranose, **2**)、1,4,6-三-*O*-没食子酰基- β -*D*-吡喃葡萄糖 (1,4,6-tri-*O*-galloyl- β -*D*-glucopyranose, **3**)、1,3,4,6-四-*O*-没食子酰基- β -*D*-吡喃葡萄糖 (1,3,4,6-tetra-*O*-galloyl- β -*D*-glucopyranose, **4**)、1,2,3,6-四-*O*-没食子酰基- β -*D*-吡喃葡萄糖 (1,2,3,6-tetra-*O*-galloyl- β -*D*-glucopyranose, **5**)、1,2,3,4,6-五-*O*-没食子酰基- β -*D*-吡喃葡萄糖 (1,2,3,4,6-penta-*O*-galloyl- β -*D*-glucopyranose, **6**)、1-*O*-没食子酰基-4,6-(*S*)-六羟基联苯甲酰基- β -*D*-吡喃型葡萄糖 [1-*O*-galloyl-4,6-(*S*)-HHDP- β -*D*-glucopyranose, **7**]、1-*O*-没食子酰基-2,3-(*S*)-六羟基联苯甲酰基- β -*D*-吡喃型葡萄糖 [1-*O*-galloyl-2,3-(*S*)-HHDP- β -*D*-glucopyranose, **8**]、1,3-二-*O*-没食子酰基-4,6-(*S*)-六羟基联苯甲酰基- β -*D*-吡喃型葡萄糖 [1,3-di-*O*-galloyl-4,6-(*S*)-HHDP- β -*D*-glucopyranose, **9**]、1,6-二-*O*-没食子酰基-2,3-(*S*)-六羟基联苯甲酰基- β -*D*-吡喃型葡萄糖 [1,6-di-*O*-galloyl-2,3-(*S*)-HHDP- β -*D*-glucopyranose, **10**]、木麻黄鞣亭 (casuarictin, **11**)、1,2,3-三-*O*-没食子酰基-4,6-(*S*)-六羟基联苯二

甲酰基- β -*D*-吡喃型葡萄糖 [1,2,3-tri-*O*-galloyl-4,6-(*S*)-HHDP- β -*D*-glucopyranose, **12**]、1,4,6-三-*O*-没食子酰基-2,3-(*S*)-六羟基联苯二甲酰基- β -*D*-吡喃型葡萄糖 [1,4,6-tri-*O*-galloyl-2,3-(*S*)-HHDP- β -*D*-glucopyranose, **13**]、hippophaeenin B (**14**)、pedunculagin (**15**)、木麻黄鞣宁 (casuarinin, **16**)、鞣花酸 (ellagic acid, **17**) 以及松醇 (pinitol, **18**)。其中，化合物 **2**、**3**、**5**、**6**、**8**、**10**、**12** 和 **13** 为首次从该属植物中分离得到；生物活性研究表明，沙棘叶中的鞣质类化合物具有较强的抗炎活性和抗肥胖活性。

1 仪器与材料

JEOL ECA 600 型核磁共振波谱仪，JEOL GC mate 质谱仪，JASCO 半制备型高效液相色谱仪，柱色谱硅胶、ODS、Sephadex LH-20 葡聚糖凝胶、MCI CHP20 吸附树脂等，半制备色谱柱 YMK Pak Ph (250 mm×10 mm)、Cosmosil 5C₁₈ PAQ (250 mm×10 mm)、Cosmosil 5C₁₈ π -NAP (250 mm×10 mm) 等，试剂均为分析纯。

实验用沙棘叶采于内蒙古，经兰州大学药学院生药学研究所马志刚教授鉴定为沙棘 *Hippophae rhamnoides* L. 的干燥叶，标本 (SJ20171001) 保存于兰州大学药学院。

2 提取与分离

沙棘叶 6 kg 用 80% 甲醇浸泡提取，反复 3 次，滤过合并提取液，减压浓缩得浸膏 1.4 kg。浸膏用水分散后，用氯仿、醋酸乙酯、正丁醇分别萃取 3 次，减压回收溶剂，得相应的提取物，其中醋酸乙酯层和水层分别为 60 g 和 933 g。取醋酸乙酯部位 57 g 浸膏，20% 甲醇溶解后，进行 Sephadex LH-20 柱色谱分离，以甲醇-水 (20:80→100:0) 溶剂系统梯度洗脱，得到 4 个部分 Fr. 1~4，Fr. 4 (20 g) 经过硅胶、MCI CHP-20 柱色谱和半制备高效液相色谱分离纯化，得到化合物 **1** (180.0 mg)、**2** (8.0 mg)、**3** (38 mg)、**4** (10 mg)、**5** (37 mg)、**6** (50 mg)、**7** (140.0 mg)、**8** (180.0 mg)、**9** (10 mg)、**10** (68 mg)、**11** (560 mg)、**12** (82 mg)、**13** (290 mg)、**15** (120.5 mg)、**16** (170.1 mg)、**17** (130.1 mg)。取水层 910 g 浸膏，用 Sephadex LH-20 柱色谱进行

分离,以甲醇-水(0:100→100:0)溶剂系统梯度洗脱,得到6个部分Fr. 1~6, Fr. 3(15 g)经过MCI CHP-20柱色谱分离纯化,得到化合物**14**(560 mg)、**16**(700.0 mg)。Fr. 1(580 g)经过MCI CHP-20柱色谱分离纯化,得到化合物**18**(1 400 mg)。

3 结构鉴定

化合物**1**: 浅褐色粉末, $[\alpha]_D^{25} -92.1^\circ$ (*c* 0.2, MeOH); FAB-MS *m/z*: 635 $[M-H]^-$, HR-FAB-MS *m/z*: 635.088 3 $[M-H]^-$ (计算值 635.088 3, $C_{27}H_{23}O_{18}$); 1H -NMR (600 MHz, acetone- d_6) δ : 5.99 (1H, d, *J* = 8.4 Hz, glu-H-1), 5.26 (1H, t, *J* = 8.8 Hz, glu-H-2), 3.99 (1H, t, *J* = 9.5 Hz, glu-H-3), 3.77 (1H, t, *J* = 9.5 Hz, glu-H-4), 3.93 (1H, m, glu H-5), 4.58 (1H, dd, *J* = 12.1, 1.8 Hz, glu-H-6 α), 4.49 (1H, dd, *J* = 12.1, 4.7 Hz, glu-H-6 β), 7.16 (2H, s, galloyl-H-2, 6), 7.10 (2H, s, galloyl-H-2, 6), 7.08 (2H, s, galloyl-H-2, 6); ^{13}C -NMR (150 MHz, acetone- d_6) δ : 93.6 (glu-C-1), 73.9 (glu-C-2), 75.6 (glu-C-3), 71.1 (glu-C-4), 76.1 (glu-C-5), 63.9 (glu-C-6), 121.7, 121.5, 120.3 (galloyl-C-1), 110.3, 110.1, 110.0 (galloyl C-2, 6), 146.1, 146.0, 145.9 (galloyl-C-3, 5), 139.6, 139.0, 138.9 (galloyl-C-4), 166.7, 166.0, 165.2 (galloyl-C = O)。以上数据与文献报道基本一致^[9], 故鉴定化合物**1**为1,2,6-三-*O*-没食子酰基- β -D-吡喃葡萄糖。

化合物**2**: 浅褐色粉末, $[\alpha]_D^{25} +22.5^\circ$ (*c* 0.5, MeOH); FAB-MS *m/z*: 635 $[M-H]^-$, HR-FAB-MS *m/z*: 635.088 4 $[M-H]^-$ (计算值 635.088 3, $C_{27}H_{23}O_{18}$); 1H -NMR (600 MHz, acetone- d_6) δ : 5.90 (1H, d, *J* = 7.9 Hz, glu-H-1), 3.89 (1H, t, *J* = 8.3 Hz, glu-H-2), 5.36 (1H, t, *J* = 9.2 Hz, glu-H-3), 3.92 (1H, t, *J* = 9.3 Hz, glu-H-4), 3.98 (1H, m, glu-H-5), 4.58 (1H, dd, *J* = 12.1, 1.7 Hz, glu-H-6 α), 4.49 (1H, dd, *J* = 12.1, 4.7 Hz, glu-H-6 β), 7.19 (2H, s, galloyl-H-2, 6), 7.19 (2H, s, galloyl-H-2, 6), 7.16 (2H, s, galloyl-H-2, 6); ^{13}C -NMR (150 MHz, acetone- d_6) δ : 95.7 (glu-C-1), 72.4 (glu-C-2), 78.8 (glu-C-3), 69.3 (glu-C-4), 75.9 (glu-C-5), 63.9 (glu-C-6), 122.1, 121.7, 120.9 (galloyl-C-1), 110.4, 110.2, 110.0 (galloyl-C-2, 6), 146.1, 146.1, 146.0 (galloyl-C-3, 5), 139.4, 139.0, 138.7 (galloyl-C-4), 166.7, 166.6, 165.4 (galloyl-C = O)。以上数据与文献报道基本一致^[10], 故鉴定化合物**2**为1,3,6-三-*O*-没食子酰基- β -D-吡喃葡萄糖。

化合物**3**: 浅褐色粉末, $[\alpha]_D^{25} +28.9^\circ$ (*c* 0.5,

MeOH); FAB-MS *m/z*: 635 $[M-H]^-$, HR-FAB-MS *m/z*: 635.088 4 $[M-H]^-$ (计算值 635.088 3, $C_{27}H_{23}O_{18}$); 1H -NMR (600 MHz, acetone- d_6) δ : 5.86 (1H, d, *J* = 8.3 Hz, glu-H-1), 3.74 (1H, t, *J* = 8.2 Hz, glu-H-2), 4.00 (1H, t, *J* = 9.3 Hz, glu-H-3), 5.27 (1H, t, *J* = 9.0 Hz, glu-H-4), 4.15 (1H, m, glu-H-5), 4.46 (1H, dd, *J* = 12.4, 1.7 Hz, glu-H-6 α), 4.20 (1H, dd, *J* = 12.4, 5.2 Hz, glu-H-6 β), 7.20 (2H, s, galloyl-H-2, 6), 7.17 (2H, s, galloyl-H-2, 6), 7.14 (2H, s, galloyl-H-2, 6); ^{13}C -NMR (150 MHz, Acetone- d_6) δ : 95.4 (glu C-1), 74.1 (glu-C-2), 75.5 (glu-C-3), 71.6 (glu-C-4), 73.9 (glu-C-5), 63.4 (glu-C-6), 121.5, 121.4, 120.8 (galloyl-C-1), 110.3, 110.2, 110.0 (galloyl-C-2, 6), 146.0, 146.0, 145.9 (galloyl-C-3, 5), 139.4, 139.0, 138.8 (galloyl-C-4), 166.4, 166.0, 165.3 (galloyl-C = O)。以上数据与文献报道基本一致^[11], 故鉴定化合物**3**为1,4,6-三-*O*-没食子酰基- β -D-吡喃葡萄糖。

化合物**4**: 浅褐色粉末, $[\alpha]_D^{25} +30.8^\circ$ (*c* 0.5, MeOH); FAB-MS *m/z*: 787 $[M-H]^-$, HR-FAB-MS *m/z*: 787.099 3 $[M-H]^-$ (计算值 787.099 2, $C_{34}H_{27}O_{22}$); 1H -NMR (600 MHz, acetone- d_6) δ : 6.01 (1H, d, *J* = 8.3 Hz, glu-H-1), 4.09 (1H, t, *J* = 8.6 Hz, glu-H-2), 5.70 (1H, t, *J* = 9.6 Hz, glu-H-3), 5.51 (1H, t, *J* = 9.6 Hz, glu-H-4), 4.41 (1H, m, glu-H-5), 4.58 (1H, dd, *J* = 12.4, 1.7 Hz, glu-H-6 α), 4.49 (1H, dd, *J* = 12.4, 5.2 Hz, glu-H-6 β), 7.21 (2H, s, galloyl-H-2, 6), 7.15 (2H, s, galloyl-H-2, 6), 7.10 (2H, s, galloyl-H-2, 6), 7.07 (2H, s, galloyl-H-2, 6); ^{13}C -NMR (150 MHz, acetone- d_6) δ : 94.8 (glu-C-1), 71.2 (glu-C-2), 75.1 (glu-C-3), 68.9 (glu-C-4), 73.0 (glu-C-5), 62.6 (glu-C-6), 120.2, 120.1, 119.4, 119.4 (galloyl-C-1), 109.6, 109.4, 109.4, 109.3 (galloyl-C-2, 6), 145.5, 145.4, 145.4, 145.3 (galloyl-C-3, 5), 139.2, 139.0, 138.5, 138.5 (galloyl-C-4), 166.21, 166.2, 165.7, 165.3 (galloyl-C = O)。以上数据与文献报道基本一致^[12], 故鉴定化合物**4**为1,3,4,6-四-*O*-没食子酰基- β -D-吡喃葡萄糖。

化合物**5**: 浅褐色粉末, $[\alpha]_D^{25} +28.1^\circ$ (*c* 0.5, MeOH); FAB-MS *m/z*: 787 $[M-H]^-$, HR-FAB-MS *m/z*: 787.099 3 $[M-H]^-$ (计算值 787.099 2, $C_{34}H_{27}O_{22}$); 1H -NMR (600 MHz, acetone- d_6) δ : 6.19 (1H, d, *J* = 8.6 Hz, glu-H-1), 5.48 (1H, t, *J* = 8.6 Hz, glu-H-2), 5.69 (1H, t, *J* = 8.9 Hz, glu-H-3), 4.11 (1H,

m, glu-H-4), 4.16 (1H, m, glu-H-5), 4.62 (1H, dd, $J = 12.1, 1.8$ Hz, glu-H-6 α), 4.58 (1H, dd, $J = 12.1, 4.7$ Hz, glu-H-6 β), 7.19 (2H, s, galloyl-H-2, 6), 7.10 (2H, s, galloyl-H-2, 6), 7.09 (2H, s, galloyl H-2, 6), 7.01 (2H, s, galloyl H-2, 6); $^{13}\text{C-NMR}$ (150 MHz, acetone- d_6) δ : 93.5 (glu-C-1), 71.8 (glu-C-2), 75.9 (glu-C-3), 68.4 (glu-C-4), 76.1 (glu-C-5), 63.7 (glu-C-6), 121.6, 121.4, 120.8, 120.1 (galloyl-C-1), 110.3, 110.2, 110.1, 110.0 (galloyl-C-2, 6), 146.1, 146.1, 145.9, 145.9 (galloyl-C-3, 5), 139.7, 139.2, 139.0, 138.9 (galloyl-C-4), 166.6, 166.2, 165.8, 165.0 (galloyl-C = O)。以上数据与文献报道基本一致^[13], 故鉴定化合物 **5** 为 1,2,3,6-四-*O*-没食子酰基- β -D-吡喃葡萄糖。

化合物 **6**: 浅褐色粉末, $[\alpha]_{\text{D}}^{25} +23.0^\circ$ (c , 0.5, MeOH); FAB-MS m/z : 939 $[\text{M}-\text{H}]^-$, HR-FAB-MS m/z : 939.110 3 $[\text{M}-\text{H}]^-$ (计算值 939.110 2, $\text{C}_{41}\text{H}_{31}\text{O}_{26}$); $^1\text{H-NMR}$ (600 MHz, acetone- d_6) δ : 6.34 (1H, d, $J = 8.5$ Hz, glu H-1), 5.62 (1H, t, $J = 8.4$ Hz, glu-H-2), 6.02 (1H, t, $J = 9.5$ Hz, glu-H-3), 5.67 (1H, t, $J = 9.5$ Hz, glu-H-4), 4.58 (1H, m, glu-H-5), 4.55 (1H, dd, $J = 12.4, 1.9$ Hz, glu-H-6 α), 4.42 (1H, dd, $J = 12.4, 4.4$ Hz, glu-H-6 β), 7.19 (2H, s, galloyl-H-2, 6), 7.12 (2H, s, galloyl-H-2, 6), 7.06 (2H, s, galloyl-H-2, 6), 7.02 (2H, s, galloyl-H-2, 6), 6.98 (2H, s, galloyl-H-2, 6); $^{13}\text{C-NMR}$ (150 MHz, acetone- d_6) δ : 93.3 (glu-C-1), 71.8 (glu-C-2), 73.3 (glu-C-3), 69.3 (glu-C-4), 74.0 (glu-C-5), 62.8 (glu-C-6), 121.4, 120.7, 120.6, 120.6, 119.9 (galloyl-C-1), 110.4, 110.3, 110.2, 110.1, 110.1 (galloyl-C-2, 6), 146.1, 146.03, 145.98, 145.94, 145.86 (C-3, 5), 139.8, 139.4, 139.3, 139.2, 139.0 (galloyl-C-4), 166.4, 165.9, 165.7, 165.6, 165.0 (galloyl-C = O)。以上数据与文献报道基本一致^[13], 故鉴定化合物 **6** 为 1,2,3,4,6-五-*O*-没食子酰基- β -D-吡喃葡萄糖。

化合物 **7**: 浅褐色粉末, $[\alpha]_{\text{D}}^{25} -26.3^\circ$ (c 0.3, MeOH); FAB-MS m/z : 633 $[\text{M}-\text{H}]^-$, HR-FAB-MS m/z : 633.072 9 $[\text{M}-\text{H}]^-$ (计算值 633.072 7, $\text{C}_{27}\text{H}_{21}\text{O}_{18}$); $^1\text{H-NMR}$ (600 MHz, acetone- d_6) δ : 5.75 (1H, d, $J = 7.9$ Hz, glu-H-1), 3.79 (1H, t, $J = 8.3$ Hz, glu-H-2), 3.93 (1H, t, $J = 9.6$ Hz, glu-H-3), 4.91 (1H, t, $J = 9.6$ Hz, glu-H-4), 4.19 (1H, m, glu-H-5), 5.22 (1H, dd, $J = 12.7, 6.2$ Hz, glu-H-6 α), 3.86 (1H, d, $J = 12.7$ Hz, glu-H-6 β), 7.24 (2H, s, galloyl-H-2, 6), 6.81,

6.66 (各 1H, s, HHDP H-3, 3'); $^{13}\text{C-NMR}$ (150 MHz, acetone- d_6) δ : 95.1 (glu-C-1), 73.1 (glu-C-2), 74.0 (glu-C-3), 71.8 (glu-C-4), 72.1 (glu-C-5), 63.0 (glu-C-6), 119.1 (galloyl-C-1), 109.6 (galloyl-C-2, 6), 145.2 (galloyl-C-3, 5), 139.2 (galloyl-C-4), 165.6 (galloyl C = O), 115.5, 115.2 (HHDP C-1, 1'), 125.4, 125.1 (HHDP C-2, 2'), 107.0, 107.4 (HHDP C-3, 3'), 144.3, 144.3 (HHDP C-4, 4'), 135.9, 135.9 (HHDP C-5, 5'), 144.0, 143.9 (HHDP C-6, 6'), 168.5, 168.2 (HHDP-C = O)。以上数据与文献报道基本一致^[14], 故鉴定化合物 **7** 为 1-*O*-没食子酰基-4,6-(*S*)-六羟基联苯甲酰基- β -D-吡喃型葡萄糖。

化合物 **8**: 浅褐色粉末, $[\alpha]_{\text{D}}^{25} -31.8^\circ$ (c , 0.3, MeOH); FAB-MS m/z : 633 $[\text{M}-\text{H}]^-$, HR-FAB-MS m/z : 633.072 5 $[\text{M}-\text{H}]^-$ (计算值 633.072 7, $\text{C}_{27}\text{H}_{21}\text{O}$); $^1\text{H-NMR}$ (600 MHz, acetone- d_6) δ : 6.13 (1H, d, $J = 8.2$ Hz, glu H-1), 5.01 (1H, t, $J = 8.6$ Hz, glu-H-2), 5.22 (1H, t, $J = 9.6$ Hz, glu-H-3), 3.96 (1H, t, $J = 9.6$ Hz, glu-H-4), 3.75 (1H, m, glu-H-5), 3.82 (1H, dd, $J = 12.1, 12.4$ Hz, glu-H-6 α), 2.92 (1H, dd, $J = 12.1, 4.8$ Hz, glu-H-6 β), 7.15 (2H, s, galloyl-H-2, 6), 6.71, 6.43 (各 1H, s, HHDP H-3, 3'); $^{13}\text{C-NMR}$ (150 MHz, acetone- d_6) δ : 92.1 (glu-C-1), 75.4 (glu-C-2), 80.3 (glu-C-3), 67.8 (glu-C-4), 75.4 (glu-C-5), 61.7 (glu-C-6), 120.2 (galloyl-C-1), 110.1 (galloyl-C-2, 6), 146.2 (galloyl-C-3, 5), 139.7 (galloyl-C-4), 165.0 (galloyl-C = O), 114.53, 114.45 (HHDP C-1, 1'), 127.0, 126.5 (HHDP C-2, 2'), 107.6, 107.1 (HHDP C-3, 3'), 145.2, 145.0 (HHDP C-4, 4'), 136.3, 136.2 (HHDP C-5, 5'), 144.5, 144.4 (HHDP C-6, 6'), 169.4, 168.7 (HHDP C = O)。以上数据与文献报道基本一致^[15], 故鉴定化合物 **8** 为 1-*O*-没食子酰基-2,3-(*S*)-六羟基联苯甲酰基- β -D-吡喃型葡萄糖。

化合物 **9**: 浅褐色粉末, $[\alpha]_{\text{D}}^{25} -45.4^\circ$ (c , 0.3, MeOH); FAB-MS m/z : 785 $[\text{M}-\text{H}]^-$, HR-FAB-MS m/z : 785.083 0 $[\text{M}-\text{H}]^-$ (计算值 785.083 6, $\text{C}_{34}\text{H}_{25}\text{O}_{22}$); $^1\text{H-NMR}$ (600 MHz, acetone- d_6) δ : 5.92 (1H, d, $J = 8.3$ Hz, glu-H-1), 3.74 (1H, t, $J = 8.2$ Hz, glu-H-2), 5.51 (1H, t, $J = 9.2$ Hz, glu-H-3), 5.07 (1H, t, $J = 10.0$ Hz, glu-H-4), 4.37 (1H, m, glu-H-5), 5.33 (1H, dd, $J = 13.4, 6.5$ Hz, glu-H-6 α), 4.20 (1H, d, $J = 13.4$ Hz, glu-H-6 β), 7.22 (2H, s, galloyl-H-2, 6), 7.05 (2H, s, galloyl-H-2, 6), 6.64, 6.44 (各 1H, s, HHDP

H-3, 3'); ^{13}C -NMR (150 MHz, acetone- d_6) δ : 95.9 (glu-C-1), 72.5 (glu-C-2), 75.6 (glu-C-3), 70.8 (glu-C-4), 72.9 (glu-C-5), 63.3 (glu-C-6), 121.4, 120.6 (galloyl-C-1), 110.4, 110.2 (galloyl-C-2, 6), 146.1, 145.8 (galloyl-C-3, 5), 139.6, 138.9 (galloyl-C-4), 166.6, 165.3 (galloyl-C = O), 115.9, 115.5 (HHDP C-1, 1'), 126.6, 126.2 (HHDP C-2, 2'), 108.1, 107.8 (HHDP C-3, 3'), 145.3, 145.2 (HHDP C-4, 4'), 136.5, 136.5 (HHDP C-5, 5'), 144.5, 144.5 (HHDP C-6, 6'), 168.0, 167.7 (HHDP C = O)。以上数据与文献报道基本一致^[16]。故鉴定化合物 **9** 为 1,3-二-*O*-没食子酰基-4,6-(*S*)-六羟基联苯甲酰基- β -*D*-吡喃型葡萄糖。

化合物 **10**: 浅褐色粉末, $[\alpha]_{\text{D}}^{25} -53.0^\circ$ (c , 0.2, MeOH); FAB-MS m/z : 785 $[\text{M}-\text{H}]^-$, HR-FAB-MS m/z : 785.084 0 $[\text{M}-\text{H}]^-$ (计算值 785.083 6, $\text{C}_{34}\text{H}_{25}\text{O}_{22}$); ^1H -NMR (600 MHz, acetone- d_6) δ : 6.22 (1H, d, $J = 8.4$ Hz, glu-H-1), 5.07 (1H, t, $J = 8.4$ Hz, glu-H-2), 5.29 (1H, t, $J = 9.5$ Hz, glu-H-3), 4.08 (1H, t, $J = 9.5$ Hz, glu-H-4), 4.09 (1H, m, glu-H-5), 4.59 (1H, dd, $J = 12.1, 1.5$ Hz, glu-H-6 α), 4.54 (1H, d, $J = 12.1, 4.0$ Hz, glu-H-6 β), 7.17 (2H, s, galloyl-H-2, 6), 7.15 (2H, s, galloyl-H-2, 6), 6.71, 6.44 (各 1H, s, HHDP H-3, 3'); ^{13}C -NMR (150 MHz, acetone- d_6) δ : 92.3 (glu-C-1), 75.5 (glu-C-2), 80.0 (glu-C-3), 76.3 (glu-C-4), 67.9 (glu-C-5), 63.5 (glu-C-6), 121.5, 120.2 (galloyl-C-1), 110.2, 110.0 (galloyl-C-2, 6), 146.2, 146.1 (galloyl-C-3, 5), 139.8, 138.9 (galloyl-C-4), 166.6, 165.0 (galloyl-C = O), 114.7, 114.5 (HHDP C-1, 1'), 127.0, 126.5 (HHDP C-2, 2'), 107.7, 107.1 (HHDP C-3, 3'), 145.2, 145.0 (HHDP C-4, 4'), 136.4, 136.3 (HHDP C-5, 5'), 144.6, 144.6 (HHDP C-6, 6'), 169.4, 168.8 (HHDP C = O)。以上数据与文献报道基本一致^[17], 故鉴定化合物 **10** 为 1,6-二-*O*-没食子酰基-2,3-(*S*)-六羟基联苯甲酰基- β -*D*-吡喃型葡萄糖。

化合物 **11**: 浅褐色粉末, $[\alpha]_{\text{D}}^{25} +31.2^\circ$ (c , 1.0, MeOH); FAB-MS m/z : 935 $[\text{M}-\text{H}]^-$, HR-FAB-MS m/z : 935.07 89 $[\text{M}-\text{H}]^-$ (计算值 935.078 9, $\text{C}_{41}\text{H}_{27}\text{O}_{26}$); ^1H -NMR (600 MHz, acetone- d_6) δ : 6.22 (1H, d, $J = 8.8$ Hz, glu-H-1), 5.19 (1H, t, $J = 8.8$ Hz, glu-H-2), 5.46 (1H, t, $J = 9.2$ Hz, glu-H-3), 5.17 (1H, t, $J = 9.9$ Hz, glu-H-4), 4.51 (1H, m, glu-H-5), 5.37 (1H, dd, $J = 12.1, 6.6$ Hz, glu-H-6 α), 4.42 (1H, d, $J = 12.1$ Hz, glu-H-6 β), 7.18 (2H, s, galloyl-H-2, 6), 6.68, 6.55,

6.47, 6.37 (1H, s, HHDP H-3, 3'); ^{13}C -NMR (150 MHz, acetone- d_6) δ : 92.3 (glu-C-1), 75.9 (glu-C-2), 77.2 (glu-C-3), 69.2 (glu-C-4), 73.5 (glu-C-5), 63.1 (glu-C-6), 120.0 (galloyl-C-1), 110.3 (galloyl-C-2, 6), 146.3 (galloyl-C-3, 5), 140.0 (galloyl-C-4), 165.0 (galloyl-C = O); 116.0, 115.8, 115.0, 114.2 (HHDP C-1, 1'), 126.5, 126.5, 126.1, 125.9 (HHDP C-2, 2'), 108.3, 107.6, 107.3, 107.3 (HHDP C-3, 3'), 145.3, 145.1 (HHDP C-4, 4'), 136.63, 136.56, 136.50, 136.2 (HHDP C-5, 5'), 144.62, 144.58, 144.58, 144.58, 144.5 (HHDP C-6, 6'), 169.2, 168.6, 168.0, 167.8 (HHDP C = O)。以上数据与文献报道基本一致^[18], 故鉴定化合物 **11** 为木麻黄鞣亭。

化合物 **12**: 淡棕色粉末, $[\alpha]_{\text{D}}^{25} +46.7^\circ$ (c , 1.0, MeOH); FAB-MS m/z : 937 $[\text{M}-\text{H}]^-$, HR-FAB-MS m/z : 937.094 8 $[\text{M}-\text{H}]^-$ (计算值 937.094 6, $\text{C}_{41}\text{H}_{29}\text{O}_{26}$); ^1H -NMR (600 MHz, acetone- d_6) δ : 6.22 (1H, d, $J = 8.3$ Hz, glu-H-1), 5.62 (1H, t, $J = 8.3$ Hz, glu-H-2), 5.87 (1H, t, $J = 9.3$ Hz, glu-H-3), 5.24 (1H, t, $J = 10.0$ Hz, glu-H-4), 4.57 (m, glu-H-5), 5.37 (1H, dd, $J = 13.4, 6.5$ Hz, glu-H-6 α), 3.91 (1H, d, $J = 13.4$ Hz, glu-H-6 β), 7.14 (2H, s, galloyl-H-2, 6), 7.03 (2H, s, galloyl-H-2, 6), 7.00 (2H, s, galloyl-H-2, 6), 6.68, 6.49 (各 1H, s, HHDP H-3, 3'); ^{13}C -NMR (150 MHz, acetone- d_6) δ : 93.6 (glu-C-1), 71.7 (glu-C-2), 73.1 (glu-C-3), 70.6 (glu-C-4), 73.0 (glu-C-5), 63.0 (glu-C-6); 120.5, 120.4, 119.8 (galloyl-C-1), 110.3, 110.1, 110.0 (galloyl-C-2, 6), 146.1, 145.9, 145.7 (galloyl-C-3, 5), 139.8, 139.2, 139.1 (galloyl-C-4), 166.2, 165.4, 164.9 (galloyl-C = O), 115.6, 115.5 (HHDP C-1, 1'), 126.4, 125.8 (HHDP C-2, 2'), 108.1, 107.7 (HHDP C-3, 3'), 144.4, 144.40 (HHDP C-4, 4'), 136.5, 136.4 (HHDP C-5, 5'), 145.2, 145.1 (HHDP C-6, 6'), 168.0, 167.5 (HHDP C = O)。以上数据与文献报道的数据一致^[19], 故鉴定化合物 **12** 为 1,2,3-三-*O*-没食子酰基-4,6-(*S*)-六羟基联苯二甲酰基- β -*D*-吡喃型葡萄糖。

化合物 **13**: 淡棕色粉末 $[\alpha]_{\text{D}}^{25} +51.0^\circ$ (c , 1.0, MeOH); FAB-MS m/z : 937 $[\text{M}-\text{H}]^-$, HR-FAB-MS m/z : 937.095 0 $[\text{M}-\text{H}]^-$ (计算值 937.094 6, $\text{C}_{41}\text{H}_{29}\text{O}_{26}$); ^1H -NMR (600 MHz, acetone- d_6) δ : 6.37 (1H, d, $J = 8.3$ Hz, glu-H-1), 5.22 (1H, t, $J = 8.9$ Hz, glu-H-2), 5.61 (1H, t, $J = 10.0$ Hz, glu-H-3), 5.63 (1H, t, $J = 10.0$ Hz, glu-H-4), 5.54 (m, glu-H-5), 4.56 (1H,

dd, $J = 12.4, 2.1$ Hz, glu-H-6 α), 4.40 (1H, dd, $J = 12.4, 4.5$ Hz, glu-H-6 β), 7.18 (2H, s, galloyl-H-2, 6), 7.17 (2H, s, galloyl-H-2, 6), 7.15 (2H, s, galloyl-H-2, 6), 6.68, 6.45 (各 1H, s, HHDP H-3, 3'); $^{13}\text{C-NMR}$ (150 MHz, acetone- d_6) δ : 92.1 (glu-C-1), 75.4 (glu-C-2), 67.9 (glu-C-3), 77.4 (glu-C-4), 74.2 (glu-C-5), 62.8 (glu-C-6); 121.3, 120.6, 120.0 (galloyl-C-1), 110.3, 110.2, 110.1 (galloyl-C-2, 6), 146.3, 146.1, 146.0 (galloyl-C-3, 5), 139.8, 139.5, 139.1 (galloyl-C-4), 166.4, 165.6, 165.0 (galloyl-C = O), 114.6, 114.4 (HHDP C-1, 1'), 126.4, 126.1 (HHDP C-2, 2'), 107.4, 107.2 (HHDP C-3, 3'), 144.6, 144.6 (HHDP C-4, 4'), 136.4 (HHDP C-5, 5'), 145.2 (HHDP C-6, 6'), 169.0, 168.6 (HHDP C = O)。以上数据与文献报道的数据一致^[17], 故鉴定化合物 **13** 为 1,4,6-三-*O*-没食子酰基-2,3-(*S*)-六羟基联苯二甲酰基- β -*D*-吡喃型葡萄糖。

化合物 **14**: 淡棕色粉末, $[\alpha]_{\text{D}}^{25} +28.0^\circ$ (c , 0.2, MeOH); FAB-MS m/z : 1 103 $[\text{M}-\text{H}]^-$, HR-FAB-MS m/z : 1 103.085 5 $[\text{M}-\text{H}]^-$ (计算值 1 103.084 8, $\text{C}_{48}\text{H}_{31}\text{O}_{31}$); $^1\text{H-NMR}$ (600 MHz, Acetone- d_6 - D_2O) δ : 5.64 (1H, d, $J = 4.8$ Hz, glu-H-1), 4.66 (1H, dd, $J = 5.2, 2.0$ Hz, glu-H-2), 5.44 (1H, dd, $J = 2.1, 2.0$ Hz, glu-H-3), 5.42 (1H, dd, $J = 8.6, 2.1$ Hz, glu-H-4), 5.29 (1H, dd, $J = 8.9, 3.4$ Hz, glu-H-4), 4.80 (1H, dd, $J = 13.0, 3.8$ Hz, glu-H-6 α), 4.02 (1H, d, $J = 13.0$ Hz, glu-H-6 β), 7.06 (2H, s, galloyl-H-2, 6), 7.11, 6.84, 6.51, 6.24 (各 1H, s, HHDP-H, valoneoyl-H); $^{13}\text{C-NMR}$ (150 MHz, acetone- d_6 - D_2O) δ : 67.4 (glu-C-1), 77.0 (glu-C-2), 69.8 (glu-C-3), 74.2 (glu-C-4), 71.0 (glu-C-5), 64.7 (glu-C-6), 120.9 (galloyl C-1), 110.1 (galloyl C-2, 6), 146.0 (galloyl C-3, 5), 139.3 (galloyl C-4), 166.0 (galloyl C = O), 115.7, 120.9, 124.5 (valoneoyl C-1, 1', 1''), 116.4, 117.1, 138.7 (valoneoyl C-2, 2', 2''), 145.3, 145.3, 145.9 (valoneoyl C-3, 3', 3''), 135.0, 136.9, 137.6 (valoneoyl C-4, 4', 4''), 145.0, 147.1, 140.2 (valoneoyl C-5, 5', 5''), 108.3, 105.0, 109.8 (valoneoyl C-6, 6', 6''), 167.6, 168.9, 168.9 (valoneoyl C = O), 120.3, 126.7 (HHDP C-1, 1'), 116.1, 116.3 (HHDP C-2, 2'), 145.9, 146.3 (HHDP C-3, 3'), 127.5, 137.0 (HHDP C-4, 4'), 143.1, 143.7 (HHDP C-5, 5'), 117.2, 105.4 (HHDP C-6, 6'), 165.0, 169.7 (HHDP C = O)。以上数据与文献报道的数据

一致^[6], 故鉴定化合物 **14** 为 hippophaenin B。

化合物 **15**: 淡棕色粉末, $[\alpha]_{\text{D}}^{25} +89.0^\circ$ (c , 0.8, MeOH); FAB-MS m/z : 783 $[\text{M}-\text{H}]^-$, HR-FAB-MS m/z : 783.068 1 $[\text{M}-\text{H}]^-$ (计算值 783.067 9, $\text{C}_{34}\text{H}_{23}\text{O}_{22}$); $^1\text{H-NMR}$ (600 MHz, acetone- d_6) δ : 5.48 (1H, t, $J = 3.7$ Hz, α -glu-H-1), 5.08 (1H, dd, $J = 9.7, 3.7$ Hz, α -glu-H-2), 5.47 (1H, t, $J = 9.7$ Hz, α -glu-H-3), 5.10 (1H, t, $J = 8.6$ Hz, α -glu-H-4), 4.62 (1H, ddd, $J = 10.1, 7.2, 1.7$ Hz, α -glu-H-5), 5.29 (1H, dd, $J = 12.1, 6.8$ Hz, α -glu-H-6 α), 3.78 (1H, dd, $J = 12.1, 1.7$ Hz, α -glu-H-6 β), 5.08 (1H, d, $J = 8.2$ Hz, β -glu-H-1), 4.85 (1H, t, $J = 8.2$ Hz, β -glu-H-2), 5.24 (1H, dd, $J = 9.2, 8.9$ Hz, β -glu-H-3), 5.08 (1H, t, $J = 9.6$ Hz, β -glu-H-4), 4.23 (1H, ddd, $J = 9.6, 6.9, 1.4$ Hz, β -glu-H-5), 5.31 (1H, dd, $J = 13.4, 6.9$ Hz, β -glu-H-6 α), 3.85 (1H, dd, $J = 13.4, 1.0$ Hz, β -glu-H-6 β), 6.68, 6.67, 6.60, 6.59, 6.56, 6.51, 6.33, 6.32 (各 1H, s, HHDP H-3, 3'); $^{13}\text{C-NMR}$ (150 MHz, acetone- d_6) δ : 91.8 (α -glu-C-1), 75.6 (α -glu-C-2), 75.8 (α -glu-C-3), 69.9 (α -glu-C-4), 67.4 (α -glu-C-5), 63.5 (α -glu-C-6), 95.5 (β -glu-C-1), 78.4 (β -glu-C-2), 77.6 (β -glu-C-3), 69.6 (β -glu-C-4), 72.5 (β -glu-C-5), 63.5 (β -glu-C-6), 115.9, 115.9, 115.8, 115.7, 115.0, 115.0, 114.0, 114.0 (HHDP C-1, 1'), 127.0, 126.8, 126.7, 126.7, 126.6, 126.2, 126.1 (HHDP C-2, 2'), 108.4, 108.3, 107.8, 107.7, 107.6, 107.5, 107.3, 107.2 (HHDP C-3, 3'), 145.2, 145.2, 145.1, 145.1, 145.1 (HHDP C-4, 4'), 136.5, 136.5, 136.0, 136.0 (HHDP C-5, 5'), 144.6, 144.5, 144.5, 144.4, 144.3, 144.3 (HHDP C-6, 6'), 169.3, 169.3, 168.8, 168.7, 168.2, 168.1, 167.8, 167.8 (HHDP C = O)。以上数据与文献报道的数据一致^[20], 故鉴定为 pedunculagin。

化合物 **16**: 淡棕色粉末 $[\alpha]_{\text{D}}^{25} +38.0^\circ$ (c , 0.8, MeOH); FAB-MS m/z : 935 $[\text{M}-\text{H}]^-$, HR-FAB-MS m/z : 935.079 1 $[\text{M}-\text{H}]^-$ (计算值 935.078 9, $\text{C}_{41}\text{H}_{27}\text{O}_{26}$); $^1\text{H-NMR}$ (600 MHz, acetone- d_6 - D_2O) δ : 5.62 (1H, d, $J = 5.2$ Hz, glu-H-1), 4.68 (1H, dd, $J = 5.2, 5.0$ Hz, glu-H-2), 5.47 (1H, t, $J = 2.0$ Hz, glu-H-3), 5.49 (1H, dd, $J = 8.0, 2.0$ Hz, glu-H-4), 5.36 (1H, dd, $J = 8.0, 2.8$ Hz, glu-H-5), 4.90 (1H, dd, $J = 13.1, 3.5$ Hz, glu-H-6 α), 4.09 (1H, d, $J = 13.1$ Hz, glu-H-6 β), 7.13 (2H, s, galloyl-H-2, 6), 6.88, 6.58, 6.53 (各 1H, s, HHDP H-3, 3'); $^{13}\text{C-NMR}$ (150 MHz,

acetone- d_6 -D₂O) δ : 67.1 (glu-C-1), 77.0 (glu-C-2), 69.8 (glu-C-3), 71.2 (glu-C-4), 74.1 (glu-C-5), 64.6 (glu-C-6), 120.6 (galloyl C-1), 110.1 (galloyl C-2, 6), 146.1 (galloyl C-3, 5), 139.6 (galloyl C-4), 166.2, 165.4, 166.4 (galloyl C = O), 116.6, 116.4, 116.2, 115.4 (HHDP C-1, 1'), 127.4, 126.8, 124.8, 119.8 (HHDP C-2, 2'), 117.3, 108.6, 107.2, 105.4 (HHDP C-3, 3'), 146.2, 145.9, 145.3, 143.9 (HHDP C-4, 4'), 139.0, 137.0, 136.1, 135.1 (HHDP C-5, 5'), 145.3, 144.8, 144.8, 143.7 (HHDP C-6, 6'), 169.9, 169.3, 168.9, 165.6 (HHDP C = O)。以上数据与文献报道的数据一致^[14], 故鉴定化合物 **16** 为木麻黄鞣宁。

化合物 **17**: 淡棕色粉末, FAB-MS m/z : 301 [M-H]⁻, HR-FAB-MS m/z : 300.998 8 [M-H]⁻ (计算值 300.998 4, C₁₄H₅O₈); ¹H-NMR (600 MHz, DMSO- d_6) δ : 7.46 (2H, s, H-5, 5'); ¹³C-NMR (150 MHz, DMSO- d_6) δ : 107.4 (C-6, 6'), 110.1 (C-5, 5'), 112.3 (C-1, 1'), 136.4 (C-2, 2'), 139.7 (C-3, 3'), 148.1 (C-4, 4'), 159.1 (C-7, 7')。以上数据与文献报道的数据一致^[21], 故鉴定化合物 **17** 为鞣花酸。

化合物 **18**: 无色粉末, FAB-MS m/z : 193 [M-H]⁻, HR-FAB-MS m/z : 193.071 0 [M-H]⁻ (计算值 193.071 1, C₉H₁₃O₆); ¹H-NMR (600 MHz, DMSO- d_6) δ : 3.31 (3H, s, OMe), 3.87 (1H, t, J = 3.4 Hz, H-1), 3.10 (1H, dd, J = 9.6, 3.1 Hz, H-2), 3.38 (1H, t, J = 9.3 Hz, H-3), 3.29 (1H, t, J = 9.3 Hz, H-4), 3.43 (1H, dd, J = 9.6, 3.9 Hz, H-5), 3.68 (1H, t, J = 3.8 Hz, H-6); ¹³C-NMR (150 MHz, DMSO- d_6) δ : 57.0 (OCH₃), 68.1 (C-1), 70.5 (C-5), 72.0 (C-6), 72.2 (C-3), 73.3 (C-4), 81.1 (C-2)。以上数据与文献报道的数据一致^[22], 故鉴定化合物 **18** 为松醇。

4 体外抗炎和抗肥胖活性评价

4.1 抑制 RAW264.7 巨噬细胞一氧化氮 (NO) 生成的抗炎活性评价

用含 10% 胎牛血清的 Ham's F12 培养基, 在 37 °C、5% CO₂ 条件下培养 RAW264.7 巨噬细胞。将溶解于 DMSO 的不同浓度的供试品、LPS (100 ng/mL) 和 IFN- γ (10 U/mL) 一同加入到细胞培养液中。培养 16 h 后, 取细胞上清培养液 100 μ L 置于新的 96 孔板中, 加入 Griess 试剂 (含 5% 磷酸的 1% 对氨基苯磺酰胺, 0.1% 萘乙二胺盐酸盐各 50 μ L)。室温下避光放置 10 min, 用酶标仪测定反应产物在 570 nm 的吸光度, 并扣除在 655 nm 的背景吸光度值。

实验结果 (表 1) 显示, 与阳性对照氨基胍相比, 多数鞣质类化合物具有较强的抑制一氧化氮生成的作用。化合物 **11**、**16** 和 **6** 的活性较强, IC₅₀ 值分别为 10.8、11.4、11.5 μ mol/L, 说明鞣质的抗炎活性可能随着没食子酰基和六羟基联苯二甲酰基的数目的增多而增强。

表 1 化合物 1~18 对脂多糖和干扰素诱导的 RAW264.7 巨噬细胞的一氧化氮 (NO) 生成的抑制率

Table 1 Inhibition on NO production stimulated by LPS and IFN- γ in RAW264.7 cells by compounds 1—18

化合物	IC ₅₀ /(μ mol·L ⁻¹)	化合物	IC ₅₀ /(μ mol·L ⁻¹)
1	21.7	11	10.8
2	16.0	12	14.9
3	19.1	13	12.3
4	14.2	14	16.8
5	15.9	15	17.6
6	11.5	16	11.4
7	18.9	17	14.0
8	17.7	18	>100
9	15.2	氨基胍	17.5
10	16.4		

4.2 抑制 3T3L-1 脂肪细胞三酰甘油 (TG) 蓄积的抗肥胖活性评价

用含 10% 新生小牛血清的高糖 DMEM 培养基, 在 37 °C、5% CO₂ 条件下培养 3T3-L1 脂肪细胞, 待细胞生长至完全融合后 2 d (第 0 天) 时, 更换成诱导分化培养基 (含 10% 胎牛血清、10 μ g/mL 胰岛素、1.0 μ mol/L 地塞米松、500 μ mol/L 1-甲基-3-异丁基黄嘌呤) 并添加不同浓度的样品培养 3 d, 换用促进分化培养基 (含 10% 胎牛血清、5 μ g/mL 胰岛素) 并添加不同浓度的样品培养至第 8 天。3T3-L1 脂肪细胞用 PBS (-) 清洗后, 用含 1 mmol/L EDTA 的 25 mmol/L Tris-HCl 缓冲液收集细胞, 超声匀浆, 用 LabAssayTM Triglyceride 试剂盒 (WAKO Pure Chemical Industries Ltd.) 测定细胞中蓄积的 TG 含量, 同时用甘油磷酸脱氢酶 (GPDH) 试剂盒 (TaKaRa Bio Inc.) 测定 GPDH 活性, 分别定量分析脂肪蓄积和分化程度, 评价供试品的抗肥胖活性。

实验结果 (图 1) 显示, 在 10 μ mol/L 浓度时, 阳性对照槲皮素对脂肪细胞 TG 蓄积和分化的抑制率约为 25%, 同浓度下的多数鞣质类化合物的抑制率为 30%~40%, 普遍较槲皮素抑制作用强。化合物

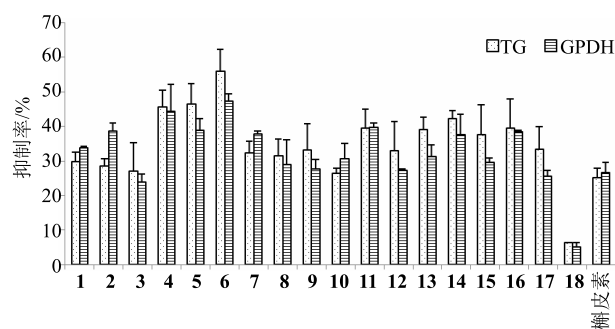


图1 化合物1~18对3T3-L1脂肪细胞的TG蓄积和GPDH分化的抑制率 ($\bar{x} \pm s, n=3$)

Fig. 1 Inhibition of TG content and GPDH activity by compounds 1—18 in 3T3-L1 adipocytes ($\bar{x} \pm s, n=3$)

4~6较1~3的抑制活性强,说明随着没食子酰基数目的增多,鞣质的抗肥胖活性增强。

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